

Synthesis and reactivity of new silyl substituted monocyclopentadienyl zirconium complexes. X-ray molecular structure of $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})_3]$

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Abstract

New silyl substituted monocyclopentadienyl complexes of Zr(IV) were synthesized from the precursor $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{Cl}_2]$ (**1**). The reaction of **1** with the lithium benzamidinate salt $\text{Li}[\text{C}(\text{Ph})\{\text{N}(\text{SiMe}_3)_2\}]\text{Cl}_2$ (**2**), which decomposes slowly in solution with elimination of SiMe_3Cl . Complex **1** reacts with alkyl, amido and alkoxo transfer reagents (4 equiv.) to afford complexes $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{X}))\text{X}_3]$ ($\text{X} = \text{NMe}_2$ (**3**), OSiMe_3 (**4**), $\text{CH}_2\text{CMe}_2\text{Ph}$ (**5**), C_6H_5 (**6**), C_6F_5 (**7**) and CH_2SiMe_3 (**8**)) in good yields. Compounds **6** and **7** retain diethyl ether used as solvent but decompose as soon as they are desolvated under high vacuum conditions. Reaction of **1** with $\text{Mg}(\text{CH}_2\text{Ph})_2 \cdot 2\text{THF}$ (4 equiv.) yields the tetrabenzyl complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})_3]$ (**9**). The ¹H and ¹³C NMR data of the latter compound are discussed in terms of the non-classical coordination mode of the CH_2Ph ligand. The molecular structure of $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})_3]$ **9** has been determined by X-ray diffraction methods. The coordination geometry around the zirconium atom shows a substituted η^5 -cyclopentadienyl ring and three different benzyl ligands: a distorted η^2 -benzyl group; a normal η^1 -benzyl group; and a benzyl ligand with an intermediate coordination mode. The benzyl fragment bonded to silicon points away from the metal center. **9** crystallized in monoclinic space group $\text{P2}_1/\text{c}$ with $a = 11.268(3)$ Å, $b = 10.846(3)$ Å, $c = 27.734(6)$ Å, $\beta = 100.29(1)^\circ$, $V = 3334.9(15)$ Å³ for $Z = 4$. The tetraalkylated compounds **6**, **7** and **9** are excellent precursors for the preparation of the chloro derivatives. Reactions of these complexes with 3 equiv. of HCl gave the corresponding trichloro $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{R}))\text{Cl}_3]$ ($\text{R} = \text{C}_6\text{H}_5$ (**10**), C_6F_5 (**11**), CH_2Ph (**12**)). The monochloro $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})_2\text{Cl}]$ (**13**) and the dichloro derivative $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})\text{Cl}_2]$ (**14**) are observed, at 60°C and 90°C, respectively, by NMR experiments in deuterated chloroform. Complexes **10** and **11** also retain coordinated solvent, decomposing slowly when it is removed. **1** and **12** in the presence of MAO as cocatalyst, at 25°C and 1 atm of monomer pressure, cause the polymerization of ethylene with moderate activities, while under similar conditions, polymerization of propylene and styrene proceeds giving only traces of atactic materials. © 1997 Elsevier Science S.A.

Keywords: Zirconium; Cyclopentadienyl complexes; Alkyl derivatives

1. Introduction

The chemistry of metallocene derivatives of group 4 metals and lanthanides has been extensively studied with a view to understanding the oligomerization and polymerization processes of unsaturated monomers. Of these processes, Ziegler–Natta α -olefin polymerization

is probably the most important [1–5]. However, the formal 12-electron monocyclopentadienyl group 4 metal complexes also play a role as catalysts in both organic synthesis and olefin polymerization [6–12]. Their reactivity profile differs considerably from those shown by their metallocene counterparts for both steric and electronic reasons. Monocyclopentadienyl complexes have been less extensively studied because fewer practical synthetic approaches exist for their preparation. Four different methods have been used in order to find a convenient preparative route for group 4 metal com-

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pounds of type $[M(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)\text{Cl}_3]$ (see Scheme 1). Route A involves the metathetical reaction of MCl_4 with the appropriate main group metal cyclopentadienide in equimolar ratio [13–18]. This procedure works well for sterically crowded cyclopentadienyl groups but is found to fail for non or less bulky substituted Cp rings for which the corresponding metallocene dichloride derivatives are obtained. The second approach (route B) is based on the photo-induced chlorination reaction of $[M(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)_2\text{Cl}_2]$ in chlorinated solvents producing, normally, very poor yields owing to the inability to control the extent of the reaction [19,20]. Route C is based on the reaction of MCl_4 with 1 equivalent of the appropriate silylated cyclopentadiene ligand. This procedure represents a particularly efficient method for the synthesis of trichloro monocyclopentadienyl titanium derivatives and seems to work quite well for the zirconium and hafnium complexes with sterically demanding Cp rings. As with route A, the use of less hindered Cp ligands affords a mixture of mono and dicyclopentadienyl compounds [21,22]. Recently, a convenient method for the synthesis of these monocyclopentadienyl complexes via ligand redistribution reactions, mixing MCl_4 and $[M(\eta^5\text{-C}_5\text{H}_{5-n}\text{R}_n)_2\text{Cl}_2]$ in an equimolar ratio (route D), has been reported [23].

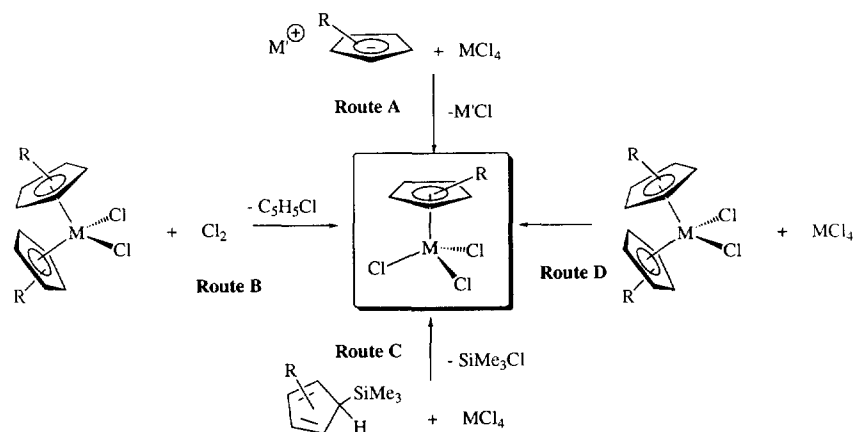
We describe in this paper the reactivity of the previously reported chlorodimethylsilyl-substituted monocyclopentadienyl zirconium trichloride complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{Cl}_3]$ [24] with alkyl, alkoxo or amido reagents. These reactions give substitution of the chlorine ligands bonded to the zirconium atom and involve a different and efficient approach to the synthesis of new silyl substituted monocyclopentadienyl zirconium derivatives by introducing side chain functionalities in the cyclopentadienyl ring. This allows for a comparison in the behaviour between the zirconium compound with the observed for the analogous titanium complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{Cl}_3]$ [24–26].

2. Results and discussion

2.1. Synthesis of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\{\text{C}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\text{Cl}_2\}$ (2) and $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{X})\}\text{X}_3]$ ($\text{X} = \text{NMe}_2$, OSiMe_3 , $\text{CH}_2\text{CMe}_2\text{Ph}$, C_6H_5 , C_6F_5 , CH_2SiMe_3 , CH_2Ph) (3–9)

The reaction of $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{Cl}_3]$ (**1**) with the lithium benzamidinate salt $\text{Li}[\text{C}(\text{Ph})\{\text{N}(\text{SiMe}_3)_2\}]$ in 1:1 molar ratio in diethyl ether at room temperature gave the corresponding $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\{\text{C}(\text{Ph})[\text{N}(\text{SiMe}_3)_2]\text{Cl}_2\}$ (**2**) as white crystals in 60% yield. This compound is moisture sensitive but thermally stable in the solid state. It can thus be stored under an inert atmosphere for long periods as a solid, but decomposes slowly in solution at room temperature to unidentified materials via SiMe_3Cl liberation. This behaviour contrasts with the higher stability shown by the analogous complex $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\{\text{N}(\text{SiMe}_3)_2\}\text{Cl}_2]$ which does not decompose even at reflux in toluene [25,26], probably due to the greater steric hindrance of the benzamidinate ligand in **2**.

Treatment of **1** with 4 equivalents of the amido or alkoxo lithium salts LiNMe_2 or LiOSiMe_3 in diethyl ether at -30°C afforded the tetraamido derivative $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{NMe}_2))(\text{NMe}_2)_3]$ (**3**) and the tetraalkoxo compound $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{OSiMe}_3)\}(\text{OSiMe}_3)_3]$ (**4**) respectively as yellow oils in high yields. Reaction of **1** with 4 equivalents of the appropriate alkyl or aryl lithium reagent in diethyl ether solutions produced the tetraalkyl or tetraaryl derivative $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{R})\}\text{R}_3]$ ($\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$ (**5**), C_6H_5 (**6**), C_6F_5 (**7**) and CH_2SiMe_3 (**8**)) in good yield. Attempts to permethylate compound **1** using LiMe or AlMe_3 as alkylating reagents were not successful. An analogous reaction of **1** with $\text{Mg}(\text{CH}_2\text{Ph})_2 \cdot 2\text{THF}$ (molar ratio 1:2) in diethyl ether



Scheme 1.

at -30°C gave the tetrabenzyl complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{Ph}))(\text{CH}_2\text{Ph})_3]$ (**9**) as bright yellow crystals in high yield. The molecular structure of **9** has been determined by X-ray crystallography and will be discussed in detail later. The reactions for the syntheses of compounds **2–9** are shown in Scheme 2.

Whereas compound **5** was obtained as a pure yellow oil, complexes **6** and **7** were isolated as brown and pale yellow crystals respectively, retaining coordinated diethyl ether. Similar behaviour has been observed for the non substituted monocyclopentadienyl zirconium complex $[\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Ph}_3]$ [19] although no etherate is formed by the analogous complex containing the bulkier and electron rich pentamethylcyclopentadienyl ligand [27]. This feature could be due to the steric and electronic requirements imposed by the silyl substituted monocyclopentadienyl ring in the zirconium complexes described in this paper. Compounds **6** and **7** decomposed when the coordinated diethyl ether was removed under high vacuum. Complex **8** was prepared using an excess of $\text{LiCH}_2\text{SiMe}_3$ (4.5–5 equiv.) and obtained as a yellow oil, always contaminated by the lithium reagent due to the high solubility of both species even in hydrocarbon solvents.

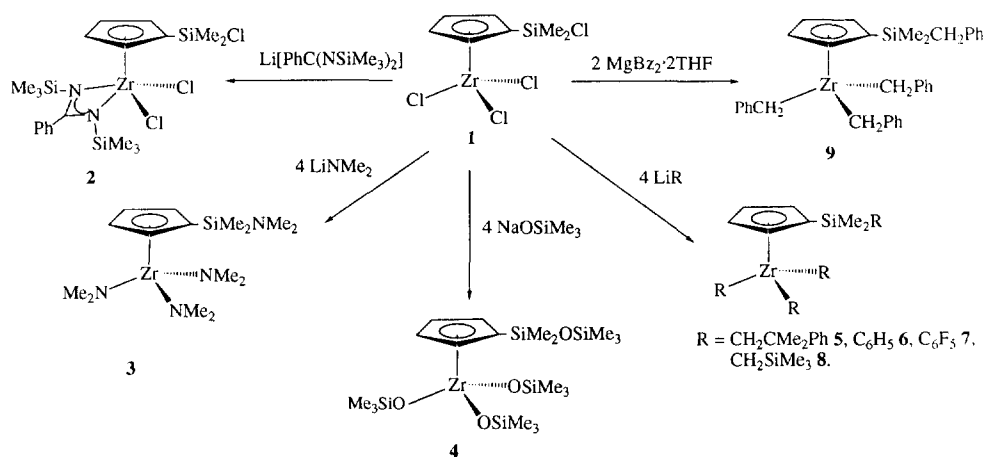
When the same reactions were carried out using appropriate molar ratios of the alkylating reagents to prepare mono-, di- or tri-substituted derivatives, intractable mixtures were obtained from which no pure substance could be isolated.

Compound **1** has two different types of chlorine atoms which may be involved in substitution reactions, namely the chlorine bonded to silicon and those bonded to the metal centre. We have previously studied the reactivity of the $\text{Zr}-\text{Cl}$ and $\text{Si}-\text{Cl}$ bonds in compound **1** towards hydrolysis, and the metathetical reaction using lithium amide reagents showing both units different degrees of reactivity. The former reaction causes the cleavage of the $\text{Si}-\text{Cl}$ bond whereas the latter gives rise to nucleophilic attack on $\text{Si}-\text{Cl}$ and $\text{Zr}-\text{Cl}$ bonds [24–

26]. Selective treatment of **1** with 1, 2 or 3 equivalents of the nucleophiles discussed in this paper produced mixtures of compounds, showing no selectivity under these conditions. This behaviour contrasts with that observed for the analogous titanium derivative $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{Cl}_3]$ where the use of three equivalents of the alkyl transfer reagent gave the $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl}))\text{R}_3]$ as the unique product [24].

The spectroscopic and analytical data for the new compounds are included in the Section 3 and will only be discussed where appropriate. The NMR spectra of compounds **3–9** show two groups of resonances, one for the substituent bonded to Si and a second group for all the amido, alkoxo or alkyl groups attached to the metal centre. Two different methylene environments are observed in the NMR spectra for **9**: for ZrCH_2Ph , resonances at δ 1.59 and 66.7 are observed in the ^1H and ^{13}C NMR spectra respectively, while for SiCH_2Ph the corresponding resonances appear at δ 2.14 and 27.7. Low temperature NMR experiments have shown no spectroscopic differences in the benzyl ligands attached to zirconium indicating that these three alkyl groups become equivalent in solution. However, in the NMR spectra at room temperature, the chemical shift of the *ortho* protons of the benzyl group $\text{Zr}-\text{CH}_2\text{Ph}$ appear at δ 6.52, shifted upfield from the normal aromatic region [13,28] and the *ipso*-C resonances for $\text{Zr}-\text{CH}_2\text{Ph}$ (δ 143.6) appear downfield from those observed for $\text{Si}-\text{CH}_2\text{Ph}$ (δ 139.5). The J_{CH} coupling constant found for $\text{Zr}-\text{CH}_2\text{Ph}$ (127.3 Hz) is slightly higher than that observed for the undistorted $\text{Si}-\text{CH}_2\text{Ph}$ (120.9 Hz). These NMR data would suggest that there is somehow, a non classical benzyl interaction in solution for the benzyl ligands bonded to zirconium [28] with no significant interactions in the side chain benzyl group attached to silicon. Similar spectroscopic behaviour has been reported for related d^0 electronically unsaturated benzyl complexes of the early transition metals [13,28–32].

The ^{19}F -NMR spectrum of compound **7** is noteworthy.

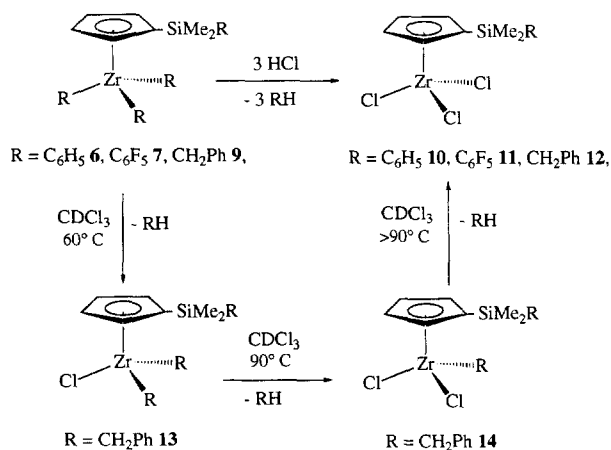


thy showing two sets of resonances attributed to the two patterns of the C_6F_5 group (δ –123.7 (br) F_{ortho} , –156.3 F_{para} , –162.3 (br) F_{meta} corresponding to the groups attached to Zr and δ –128.4 F_{ortho} , –152.3 F_{para} , –162.6 F_{meta} corresponding to the one linked to silicon).

2.2. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2R))Cl_3]$ ($R = C_6H_5$ (**10**), C_6F_5 (**11**), CH_2Ph (**12**))

Reactions of hexane solutions of **6**, **7** and **9** with 3 equivalents of HCl in diethyl ether at room temperature, afforded the trichloro derivatives $[Zr(\eta^5-C_5H_4(SiMe_2R))Cl_3]$ ($R = C_6H_5$ (**10**), C_6F_5 (**11**), CH_2Ph (**12**)) in good yields (Scheme 3). Complexes **10–12** retained diethyl ether from the solvent mixture, decomposing on desolvation at low pressure. All these compounds are rather insoluble in hexane, slightly soluble in toluene but very soluble in chlorinated solvents. In contrast, decomposition occurs when compounds **3–5** are treated in the same manner with HCl. The 1H and ^{13}C NMR spectroscopic data for complexes **10–12** show the expected features for undistorted Si–R groups, ruling out an intramolecular coordination of the pendant aromatic groups to the metal center [31–33].

Compound **12** can also be prepared from **9** in chlorinated solvents. An NMR scale reaction of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))(CH_2Ph)_3]$ (**9**) in deuterated chloroform at 60°C led selectively to the monochloro derivative $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))(CH_2Ph)_2Cl]$ (**13**). The 1H NMR spectrum of complex **13** shows an AB spin system for the diastereotopic CH_2 protons (δ_A 1.76 and δ_B 2.01) of the Zr– CH_2Ph groups with a J_{HH} coupling constant of 10.2 Hz, whereas the *ortho* proton resonance of the aromatic ring appears at δ 6.6. Therefore, some π -aromatic benzyl-metal interaction can be proposed for this molecule [28,34]. Heating the chloroform solution above 60°C, resulted in further substitution of benzyl groups bonded to zirconium, affording a mixture of the dichloro derivative $[Zr(\eta^5-$



Scheme 3.

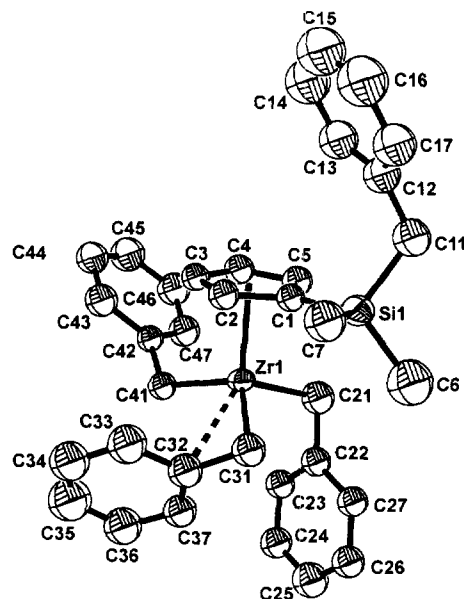


Fig. 1. Ortep view of molecular structure of compound **9** with the atom-numbering scheme. Thermal ellipsoids are given with a 40% probability.

$C_5H_4(SiMe_2CH_2Ph))(CH_2Ph)Cl_2]$ (**14**) and the trichloro compound **12**. The 1H NMR spectrum of compound **14** exhibits only one singlet at δ 2.65 for the Zr– CH_2Ph group since of the prochiral environment observed in complex **13** is lost, and no resonances below δ 6.8 could be detected for the *ortho* protons of the phenyl group. Above 90°C the mixture was totally converted to complex **12** (Scheme 3). Attempts to isolate compounds **13** and **14** on a preparative scale have been unsuccessful at the moment.

Complexes **1**, **9** and **12** in the presence of MAO or $B(C_6F_5)_3$ as cocatalyst polymerize ethylene with low activity under mild conditions (room temperature, monomer pressure 1 atm, Al/Zr = 1000, B/Zr = 1). These low activities may be due to the short life time of the Al-free catalyst system found in NMR experiments.³ Polymerization of propylene and styrene were performed under similar conditions. In each case only traces of waxy and solid material were found for polypropylene and polystyrene respectively, which were identified by ^{13}C NMR as atactic polymers.

2.3. Description of the crystal structure of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))(CH_2Ph)_3]$ (**9**)

Fig. 1 shows an ORTEP view of **9** along with the numbering scheme used. Selected bond lengths and

³ An NMR scale reaction of compound **9** with 1 equivalent of $B(C_6F_5)_3$ in CD_2Cl_2 at –78°C yielded the expected compound $\{Zr[C_5H_4(SiMe_2CH_2Ph)](CH_2Ph)_2\}^+ [B(CH_2Ph)B(C_6F_5)_3]^-$ as minor component of a blend of complexes. Further studies are in progress to investigate the nature of the mixture.

Table 1
Selected bond distances (Å) and bond angles (°) for compound 9

Zr(1)–C(21)	2.260 (19)	Zr(1)–C(31)	2.288 (17)
Zr(1)–C(32)	2.644 (21)	Zr(1)–C(41)	2.276 (14)
Si(1)–C(1)	1.863 (16)	Si(1)–C(6)	1.887 (22)
Si(1)–C(7)	1.828 (18)	Si(1)–C(11)	1.867 (21)
C(11)–C(12)	1.495 (28)	Si(21)–C(22)	1.454 (22)
C(31)–C(32)	1.471 (28)	C(41)–C(42)	1.506 (22)
Zr(1)–Cp1	2.260		
C(21)–Zr(1)–C(31)	108.5 (6)	C(21)–Zr(1)–C(32)	123.1 (6)
C(21)–Zr(1)–C(41)	101.9 (6)	C(31)–Zr(1)–C(41)	119.6 (6)
C(32)–Zr(1)–C(41)	86.0 (6)	C(1)–Si(1)–C(6)	111.9 (8)
C(1)–Si(1)–C(7)	110.3 (8)	C(6)–Si(1)–C(7)	110.5 (10)
C(1)–Si(1)–C(11)	107.0 (8)	C(6)–Si(1)–C(11)	106.8 (10)
C(7)–Si(1)–C(11)	110.4 (9)	Si(1)–C(11)–C(12)	114.7 (15)
Zr(1)–C(21)–C(22)	102.0 (13)	Zr(1)–C(31)–C(32)	86.5 (10)
Zr(1)–C(32)–C(31)	59.8 (10)	Zr(1)–C(41)–C(42)	122.4 (11)
Cp(1)–Zr(1)–C(21)	107.4	Cp(1)–Zr(1)–C(31)	110.7
Cp(1)–Zr(1)–C(32)	123.8	Cp(1)–Zr(1)–C(41)	108.1

angles with their standard deviations are listed in Table 1. The metal is coordinated to a substituted η^5 -cyclopentadienyl ring and three benzyl ligands, maintaining a mononuclear environment with the classical ‘three-legged piano stool’ configuration.

In this case however, we found an asymmetrical arrangement for the legs, shown by the angles $C\alpha$ –Zr– $C\alpha$, whose values ranged from $119.6(6)^\circ$ for C31–Zr–C41 to $101.9(6)^\circ$ for C21–Zr–C41. These differences are due to the different solid state bond modes of the three benzyl groups bonded to the Zr atom. The group bonded through C31 shows a Zr–C–Ph angle of

$86.5(10)^\circ$ resulting from the closer proximity of the associated phenyl ring, in particular the *ipso* carbon, to the zirconium atom (Zr–C32 distance is $2.644(21)$ Å). This situation is ascribed to η^2 -coordination of the benzylic fragment. Comparable angle values have been found in the sterically crowded aryl oxide $[Zr(OC_6H_3Bu_2)(CH_2Ph)_3]$ (84°) [28] and in the electronically deficient cationic derivatives $[Zr(CH_2Ph)_3\{B(CH_2Ph)(C_6F_5)_3\}]^+$ (82.7°) [35] and $[Zr(C_5H_5)_2(CH_2Ph)(CH_3CN)]^+$ (84.9°) [36], although the angle is smaller than those reported in the cyclopentadienyl ring free complex $[Zr(CH_2Ph)_4(dmpe)]$ ($94.2(4)^\circ$) [37] and the related monocyclopentadienyl compound $[Zr(C_5H_5)(CH_2Ph)_3]$ ($94.5(5)^\circ$) [38]. The second benzyl ligand bonded to the metal through C41 has a Zr–C–Ph angle of $122.4(11)^\circ$, consistent with a normal η^1 -bonding mode. The third benzyl ligand has a Zr–C–Ph angle of $102.0(13)^\circ$ suggesting an intermediate interaction between the aromatic fragment and the metal centre. Several transition metal complexes showing different modes of ligation of the benzyl ligands have been structurally characterized [28,38–40]. The three $C\alpha$ atoms are bonded to Zr at the same distance, 2.27 Å (average value) and define a plane almost parallel to the Cp ring plane. Two of the phenyl rings are pointing downwards toward the metal, and their planes are almost perpendicular to the Cp ring plane. However, the phenyl group attached to C41 is pointing upwards and makes an angle of $38.5(5)^\circ$ with the Cp ring plane. This is in contrast to $CpZr(CH_2Ph)_3$ [38]

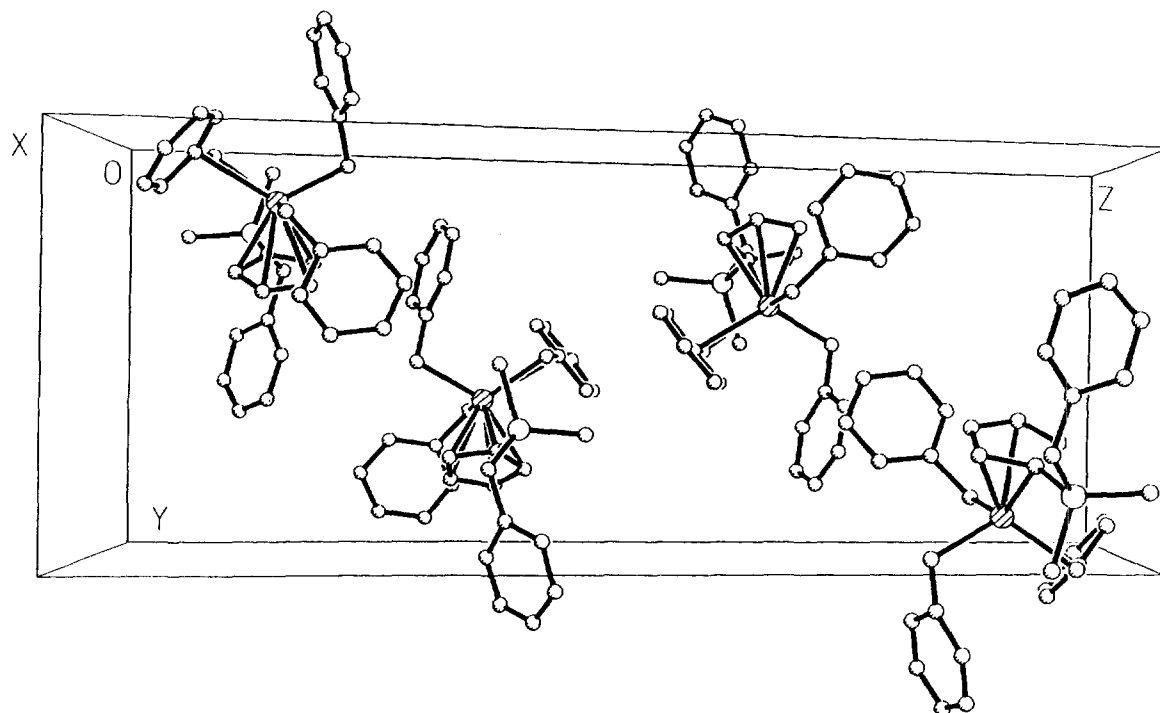


Fig. 2. Unit cell packing for the structure of compound 9.

where all the benzyl groups point down and are symmetrically placed, and to $\text{Cp}^* \text{Ti}(\text{CH}_2\text{Ph})_3$ [29,30] where the phenyl groups are symmetrically located with one of the phenyl rings pointing up, but with its plane parallel to the Cp plane.

The Cp ring is unexceptional with a Zr–Cp bond length of 2.26 Å and an average Zr–C distance of 2.49 Å. [13,41,42]. The benzyldimethylsilyl substituent of the cyclopentadienyl ring is bent away from the metal in the solid state and shows no interaction with the metal centre, in accordance with its NMR spectra in solution. The silicon atom is located 0.198(5) Å above the Cp ring plane. The Si–C–Ph angle of 114.7(15)° corresponds to a normal η^1 -benzyl ligand [43–48].

These structural features, together with the spectroscopic data observed in the NMR studies, show us that the benzyl groups are very versatile ligands. Their different ways of bonding have similar energies, so that besides electronic effects, small packing forces in the solid state have a marked influence on the differences between them. In the unit cell of compound **9** (Fig. 2) a face to face disposition of the ring bonded to C31 is observed, probably required by the η^2 bonding mode of the benzylic fragment.

3. Experimental section

3.1. General considerations

All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox model HE-63 or MBraun. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium–potassium alloy for hexane and sodium–benzophenone for diethyl ether). The lithium benzamidinate salt [49], the lithium reagents LiR ($\text{R} = \text{CH}_2\text{CMe}_2\text{Ph}$ [50], C_6H_5 , $^4\text{C}_6\text{F}_5$ [51], CH_2SiMe_3 [50]) and $\text{Mg}(\text{CH}_2\text{Ph})_2 \cdot 2\text{THF}$ [52] were prepared by known procedures. LiNMe_2 , LiOSiMe_3 and 1 M HCl solution in diethyl ether were purchased from Aldrich. C, H and N microanalyses were performed on a Perkin–Elmer 240B and/or Heraeus CHN–O–Rapid microanalyzer. Complexes **6** and **7** were always obtained with variable amounts of diethyl ether and compound **8** was repeatedly obtained contaminated with $\text{LiCH}_2\text{SiMe}_3$, making their complete analytical characterization impossible. NMR spectra, measured at 25°C, were recorded on a Varian Unity 300 (^1H NMR at 300 MHz, ^{13}C NMR at 75 MHz, and ^{19}F NMR at 282 MHz) spectrometer. ^1H and ^{13}C chemical shifts are

reported in δ units relative to TMS standard, ^{19}F chemical shifts were referenced to CCl_3F .

3.2. Synthesis of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{Cl})\}\text{-}\{\text{C}(\text{Ph})[\text{N}(\text{SiMe}_3)]_2\}\text{Cl}_2]$ (**2**)

A solution of $\text{Li}[\text{C}(\text{Ph})\{\text{N}(\text{SiMe}_3)_2\}]$ (0.38 g, 1.40 mmol) in toluene (15 ml) was added to 0.5 g of **1** (1.41 mmol) in toluene (40 ml) at -30°C . The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed under vacuum and the residue was extracted into hexane (2×35 ml) and the extracts filtered. The volume of the filtrate was reduced to ca. 20 ml and cooled to -36°C to give **2** as off-white crystals (0.49 g, 60% yield). Anal. Calcd. for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{Si}_3\text{Zr}$: C, 41.17; H, 5.66; N, 4.80. Found: C, 40.91, H, 5.57; N, 4.62. ^1H NMR (C_6D_6): δ 6.9–6.7 (m, 5H, C_6H_5), 6.78 (t, 2H, $J_{\text{HH}} = 2.56$ Hz, C_5H_4), 6.52 (t, 2H, $J_{\text{HH}} = 2.56$ Hz, C_5H_4), 0.95 (s, 6H, SiMe_2), -0.04 (s, 18H, SiMe_3).

3.3. Synthesis of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{NMe}_2)\}(\text{NMe}_2)_3]$ (**3**)

0.21 g of LiNMe_2 (4.16 mmol) was added to a diethyl ether solution (40 ml) containing 0.37 g of **1** (1.04 mmol) at -78°C . After warming to room temperature the reaction mixture was stirred for 12 h. The volatiles were removed under reduced pressure and the residue was extracted into hexane (40 ml). After filtration, solvent was removed under vacuum to give **3** as an analytically pure yellow oil (0.28 g, 71% yield). Anal. Calcd. for $\text{C}_{15}\text{H}_{34}\text{N}_4\text{SiZr}$: C, 46.24; H, 8.73; N, 14.38. Found: C, 45.91, H, 8.60; N, 14.01. ^1H NMR (C_6D_6): δ 6.32 (broad, 2H, C_5H_4), 6.29 (broad, 2H, C_5H_4), 2.94 (s, 18H, 3 Zr– NMe_2), 2.43 (s, 6H, Si-NMe_2), 0.34 (s, 6H, SiMe_2). ^{13}C NMR (C_6D_6): δ 118.1 (CH of C_5H_4), 113.9 (CH of C_5H_4), 45.4 (Zr– NMe_2), 38.3 (Si-NMe_2), -1.25 (SiMe_2).

3.4. Synthesis of $[\text{Zr}\{\eta^5\text{-C}_5\text{H}_4(\text{SiMe}_2\text{OSiMe}_3)\}\text{-}(\text{OSiMe}_3)_3]$ (**4**)

0.37 g of LiOSiMe_3 (3.82 mmol) was added to a diethyl ether solution (40 ml) containing 0.34 g of **1** (0.95 mmol) at -78°C . The reaction mixture was warmed to room temperature and stirred for 12 h giving a yellow solution. The volatiles were removed under reduced pressure and the residue was extracted into hexane (30 ml). After filtration solvent was removed from the resulting solution under vacuum to give **4** as a yellow oil (0.33 g, 64% yield). ^1H NMR (C_6D_6): δ 6.65 (t, 2H, $J_{\text{HH}} = 2.40$ Hz, C_5H_4), 6.39 (t, 2H, $J_{\text{HH}} = 2.40$ Hz, C_5H_4), 0.51 (s, 6H, SiMe_2), 0.17 (s, 27H, 3 Zr– OSiMe_3), 0.12 (s, 9H, Si-OSiMe_3).

⁴ In a typical experiment IC_6H_5 in hexane was treated with 1 equivalent of LiBut . The solvent was reduced to the half volume affording LiC_6H_5 as a white solid.

3.5. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2CMe_2Ph))-(CH_2CMe_2Ph)_3]$ (**5**)

A diethyl ether solution of **1** (0.53 g, 1.49 mmol) was treated with a diethyl ether solution of $LiCH_2CMe_2Ph$ (0.83 g, 5.97 mmol) at $-78^\circ C$. The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were completely removed under reduced pressure and the residue was extracted into hexane (40 ml). The solution was filtered and the solvent was removed under reduced pressure to give **5** as brownish orange oil (0.93 g, 84% yield). Anal. Calcd. for $C_{47}H_{62}SiZr$: C, 75.68; H, 8.32. Found: C, 75.34; H, 8.20. 1H NMR (C_6D_6): δ 7.34 (d, 2H, $J_{HH} = 1.20$ Hz, $Si-CH_2CMe_2C_6H_5$ *ortho*), 7.32 (d, 6H, $J_{HH} = 1.20$ Hz, 3 $Zr-CH_2CMe_2C_6H_5$ *ortho*), 7.28–7.09 (m, 12H, Si - and 3 $Zr-CH_2C_6H_6$ *para* and *meta* are overlapped), 5.73 (t, 2H, $J_{HH} = 2.55$ Hz, C_5H_4), 5.59 (t, 2H, $J_{HH} = 2.55$ Hz, C_5H_4), 1.34 (s, 18H, 3 $Zr-CH_2CMe_2C_6H_5$), 1.26 (s, 6H, $Si-CH_2CMe_2C_6H_5$), 1.23 (s, 2H, $Si-CH_2$), 0.99 (s, 6H, 3 $Zr-CH_2$), 0.00 (s, 6H, $SiMe_2$). ^{13}C NMR (C_6D_6): δ 152.6 ($Zr-CH_2CMe_2C_6H_5$ *ipso*), 150.8 ($Si-CH_2CMe_2C_6H_5$ *ipso*), 128.4 ($Zr-CH_2CMe_2C_6H_5$ *ortho*, $J_{CH} = 159.35$ Hz), ($Si-CH_2CMe_2C_6H_5$ *ortho*, *meta* and *para* and $Zr-CH_2CMe_2C_6H_5$ *para* are overlapped), 125.9 ($Zr-CH_2CMe_2C_6H_5$ *meta*, $J_{CH} = 155.7$), (C_5H_4 *ipso* obscured by phenyl groups), 115.7 (CH of C_5H_4 , $J_{CH} = 170.3$ Hz), 113.9 (CH of C_5H_4 , $J_{CH} = 170.3$ Hz), 92.4 ($Zr-CH_2$, $J_{CH} = 105.3$ Hz), 42.4 ($Zr-CH_2CMe_2C_6H_5$), 37.4 ($Si-CH_2CMe_2C_6H_5$), 35.4 ($Si-CH_2$), 34.3 ($Zr-CH_2CMe_2C_6H_5$), 32.6 ($Si-CH_2CMe_2C_6H_5$), 0.1 ($SiMe_2$).

3.6. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2Ph))Ph_3](Et_2O)_{0.5}$ (**6**)

0.94 g of $LiPh$ (10.92 mmol) was added to a diethyl ether solution (50 ml) containing 0.97 g of **1** (2.73 mmol) at $-78^\circ C$. The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure to give a black oil which was extracted into 50 ml of hexane. After filtration the solvent was removed from the extract, giving **6** as a dark brown oil. Recrystallization from hexane afforded **6** as brown crystals (0.73 g, 45% yield). 1H NMR (C_6D_6): δ 7.65 (d, 6H, $J_{HH} = 6.22$ Hz, 3 $Zr-C_6H_5$), 7.42–6.87 (m broad, 14H, $Si-C_6H_5$ *ortho*, *meta*, and *para* and $Zr-C_6H_5$ *meta* and *para*), 6.59 (t, 2H, $J_{HH} = 2.56$ Hz, C_5H_4), 6.27 (t, 2H, $J_{HH} = 2.56$ Hz, C_5H_4), 3.25 (q, 2H, $O-CH_2$), 1.11 (t, 3H, $O-CH_2-C-H_3$), 0.30 (s, 6H, $SiMe_2$).

3.7. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2C_6F_5))-(C_6F_5)_3](Et_2O)_2$ (**7**)

A solution of **1** (0.34 g, 0.97 mmol) in diethyl ether (25 ml) was added to a suspension of $Li(C_6F_5)$ (0.71 g,

4.08 mmol), in 15 ml of hexane at $-78^\circ C$. The reaction mixture was stirred at $-78^\circ C$ for 1 h. After warming to room temperature and allowed to stand for 6 h, the volatiles were removed under reduced pressure and the residue was extracted into hexane (40 ml). After filtration the resulting solution was evaporated under reduced pressure to 10–15 ml. By cooling at $-20^\circ C$, compound **7** was obtained as a pale brown solid, which melted at room temperature (0.83 g, 81% yield). 1H NMR (C_6D_6): δ 7.45 (broad, 2H, C_5H_4), 6.90 (broad, 2H, C_5H_4), 3.11 (q, 8H, $O-CH_2$), 0.91 (t, 12H, $O-CH_2-C-H_3$), 0.35 (s, 6H, $SiMe_2$). ^{13}C NMR (C_6D_6): δ 150.6–134.7 (C_6F_5 *ortho*, *meta* and *para*), 125.3 (C_5H_4 *ipso*), 124.2 (CH of C_5H_4), 121.1 (CH of C_5H_4), 66.1 (OCH_2CH_3), 14.0 (OCH_2CH_3), 1.3 ($SiMe_2$). ^{19}F NMR (C_6D_6): δ -123.7 (broad, 6F, $Zr-C_6F_5$ *ortho*), -128.4 (d, 2F, $J_{FF} = 17.4$ Hz, $Si-C_6F_5$ *ortho*), -152.4 (t, 1F, $J_{FF} = 20.3$ Hz, $Si-C_6F_5$ *para*), -156.3 (t, 3F, $J_{FF} = 20.34$ Hz, $Zr-C_6F_5$ *para*), -162.3 (broad, 6F, $Zr-C_6F_5$ *meta*), -162.6 (t, 2F, $Si-C_6F_5$ *meta*).

3.8. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2SiMe_3))-(CH_2SiMe_3)_3]$ (**8**)

0.42 g of $LiCH_2SiMe_3$ (4.52 mmol) was added to a diethyl ether solution (60 ml) containing 0.321 g of **1** (0.90 mmol) at $-78^\circ C$. The reaction mixture was warmed to room temperature and then stirred for 36 h. After filtration, the volatiles were removed under reduced pressure to give a waxy yellow solid which was extracted into hexane. Removal of the solvent gave **8** as very sticky solid contaminated with $LiCH_2SiMe_3$. 1H NMR (C_6D_6): δ 6.44 (t, 2H, $J_{HH} = 2.20$ Hz, C_5H_4), 5.94 (t, 2H, $J_{HH} = 2.20$ Hz, C_5H_4), 1.11 (s, 2H, $Si-CH_2$), 0.36 (s, 6H, 3 $Zr-CH_2$), 0.20 (s, 27H, 3 $Zr-CH_2-SiMe_3$), 0.04 (s, 9H, $Si-CH_2-SiMe_3$), -0.00 (s, 2H, $SiMe_2$).

3.9. Synthesis of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))-(CH_2Ph)_3]$ (**9**)

1.97 g of $Mg(CH_2Ph)_2 \cdot 2THF$ (5.6 mmol) was added to a diethyl ether solution (60 ml) containing 1 g of **1** (2.8 mmol) at $-78^\circ C$. The reaction mixture was warmed to room temperature and then stirred for 17 h. Volatiles were removed under reduced pressure, the residue extracted into toluene (2×50 ml) and the extracts filtered. The volume of the filtrate was reduced (ca. 20 ml). Crystals just began to form by cooling to $-36^\circ C$ to give **9** as bright yellow crystals (0.90 g, 56% yield). Anal. Calcd. for $C_{35}H_{38}SiZr$: C, 74.13; H, 6.74. Found: C, 74.18; H, 6.52. 1H NMR (C_6D_6): δ 7.18–6.92 (m, 12H, C_6H_5 *meta* and *para*), 6.88 (d, 2H, $J_{HH} = 7.32$ Hz, $Si-CH_2C_6H_5$ *ortho*), 6.52 (d, 6H, $J_{HH} = 7.32$ Hz, $Zr-CH_2C_6H_5$ *ortho*), 5.86 (t, 2H, $J_{HH} = 2.56$ Hz, C_5H_4), 5.55 (t, 2H, $J_{HH} = 2.56$ Hz, C_5H_4),

2.14 (s, 2H, Si-CH₂), 1.59 (s, 6H, 3 Zr-CH₂), 0.15 (s, 6H, SiMe₂). ¹³C NMR (C₆D₆): δ 143.6 (Zr-CH₂C₆H₅ *ipso*), 139.5 (Si-CH₂C₆H₅ *ipso*), 129.6 (Zr-CH₂C₆H₅ *ortho*), (Si-CH₂C₆H₅ *ortho*, *para* and Zr-CH₂C₆H₅ *para* are overlapped by the solvent), 124.7 (Si-CH₂C₆H₅ *meta*, *J*_{CH} = 161.18 Hz), 123.7 (Zr-CH₂C₆H₅ *meta*, *J*_{CH} = 161.18 Hz), 120.5 (C₅H₄ *ipso*), 118.3 (CH of C₅H₄), 116.4 (CH of C₅H₄), 66.7 (Zr-CH₂, *J*_{CH} = 127.3 Hz), 27.7 (Si-CH₂, *J*_{CH} = 120.9 Hz), -2.3 (SiMe₂).

3.10. Synthesis of [Zr(η⁵-C₅H₄(SiMe₂Ph))Cl₃] (10)

2.88 ml of 1 M solution of HCl in diethyl ether (2.88 mmol) was added to a solution of **6** (0.50 g, 0.96 mmol) in hexane at -70°C. The mixture was warmed to room temperature and then stirred for 5 h. The volatiles were concentrated and cooled to -40°C giving **10** as a yellow sticky solid (0.7 g, 21% yield). Anal. Calcd. for C₁₃H₁₅Cl₃SiZr: C, 39.33; H, 3.78. Found: C, 39.51; H, 3.85. ¹H NMR (CDCl₃): δ 7.60–6.61 (m, 5H, C₆H₅), 6.55 (t, 2H, *J*_{HH} = 2.56 Hz, C₅H₄), 6.24 (t, 2H, *J*_{HH} = 2.56 Hz, C₅H₄), 0.57 (s, 6H, SiMe₂).

3.11. Synthesis of [Zr(η⁵-C₅H₄(SiMe₂C₆F₅))Cl₃](Et₂O)_{0.5} (11)

5.65 ml of an 1 M HCl diethyl ether solution (5.65 mmol) was added to an hexane solution (45 ml) containing 1.94 g of **7** (1.88 mmol) at -60°C. The mixture was warmed to room temperature and stirred for 7 h. The resulting suspension was concentrated and cooled to -40°C to give **11** as grey powder (0.32 g, 34% yield). Anal. Calcd. for C₁₅H₁₅Cl₃SiF₅Zr: C, 34.38; H, 2.86. Found: C, 34.52; H, 2.97. ¹H NMR (CDCl₃): δ 6.87 (broad, 2H, C₅H₄), 6.79 (broad, 2H, C₅H₄), 3.54 (q, 2H, O-CH₂CH₃), 1.20 (t, 3H, O-CH₂-CH₃), 0.79 (s, 6H, SiMe₂). ¹³C NMR (CDCl₃): δ 148.4 (C₆F₅ *ortho*, *J*_{CF} = 238.1 Hz), 142.1 (C₆F₅ *para*, *J*_{CF} = 252.8 Hz), 137.2 (C₆F₅ *meta*, *J*_{CF} = 261.9 Hz), (C₆F₅ *ipso* and C₅H₄ *ipso* are obscured by the solvent), 126.7 (CH of C₅H₄), 123.8 (CH of C₅H₄), 66.0 (OCH₂CH₃), 14.9 (OCH₂CH₃), -0.71 (SiMe₂). ¹⁹F NMR (CDCl₃): δ -127.3 (d, 2F, *J*_{FF} = 15.5 Hz, C₆F₅ *ortho*), -152.8 (broad, 1F, C₆F₅ *para*), -162.7 (broad, 2F, C₆F₅ *meta*).

3.12. Synthesis of [Zr(η⁵-C₅H₄(SiMe₂CH₂Ph))Cl₃] (12)

5.69 ml of an 1 M solution of HCl in diethyl ether (5.69 mmol) was added to a solution of **9** (1.09 g, 1.89 mmol) in hexane at -70°C. The reaction mixture was warmed to room temperature and then stirred for 15 h. The volatiles were concentrated and cooled to -40°C

giving **12** as off-white solid (0.65 g, 84% yield). Anal. Calcd. for C₁₄H₁₇Cl₃SiZr: C, 40.92; H, 4.14. Found: C, 40.80; H, 4.87. ¹H NMR (CDCl₃): δ 7.16–6.81 (m, 5H, C₆H₅), 6.93 (t, 2H, *J*_{HH} = 2.56 Hz, C₅H₄), 6.68 (t, 2H, *J*_{HH} = 2.56 Hz, C₅H₄), 2.26 (s, 2H, CH₂), 0.33 (s, 6H, SiMe₂). ¹³C NMR (CDCl₃): δ 138.9 (C₆H₅ *ipso*), 132.1 (C₅H₄ *ipso*), 128.25, 128.1 (C₆H₅ *ortho* and *meta*), 126.75 (C₆H₅ *para*), 124.6 (CH of C₅H₄), 124.3 (CH of C₅H₄), 27.1 (CH₂), -2.79 (SiMe₂).

3.13. NMR scale reaction of **9** with CDCl₃

50 mg of complex **9** and 0.7 ml of deuterated chloroform, CDCl₃, were sealed in a NMR tube under argon, and heated at 60°C for 4 days. After this time the formation of compound **13** was observed. Increasing the temperature through the range of 60–90°C afforded a mixture of the dichloride **14** and the trichloride **12**. Above 90°C, the mixture was quickly and quantitatively transformed to **12**.

[Zr(η⁵-C₅H₄(SiMe₂CH₂Ph))(CH₂Ph)₂Cl] **13**: ¹H NMR (CDCl₃): δ 7.76–7.00 (9H, C₆H₅ *para* and *meta*), 6.89 (d, 2H, *J* = 6.96 Hz, Si-CH₂C₆H₅ *ortho*), 6.54 (d, 4H, *J* = 6.96 Hz, 2 Zr-CH₂C₆H₅ *ortho*), 6.23 (t, 2H, C₅H₄), 6.16 (t, 2H, C₅H₄), 2.25 (s, 2H, Si-CH₂), 2.01 (d, 2H, *J*_{HH} = 10.2 Hz, Zr-CH₂), 1.76 (d, 2H, *J*_{HH} = 10.2 Hz, Zr-CH₂), 0.21 (s, 6H, SiMe₂).

[Zr(η⁵-C₅H₄(SiMe₂CH₂Ph))(CH₂Ph)Cl₂] **14**: ¹H NMR (CDCl₃): δ 7.34–6.77 (m, 10H, C₆H₅), 6.59 (t, 2H, C₅H₄), 6.54 (t, 2H, C₅H₄), 2.65 (s, 2H, Zr-CH₂), 2.29 (s, 2H, Si-CH₂), 0.27 (s, 6H, SiMe₂).

3.14. Polymerization experiments

Polymerization of ethylene was carried out in 200-ml magnetically stirred glass flasks, which were charged with toluene (100 ml). The solvent was maintained at 25°C and saturated with the monomer at 1 atm. Polymerization runs were then initiated by injecting a toluene solution of catalyst (9.7 × 10⁻⁶ mol) and cocatalyst (Al/Zr = 1000, B/Zr = 1), while the monomer pressure was kept constant, and terminated by injecting methanol/HCl. The reaction mixture was poured into acidified methanol, washed with methanol and diethyl ether and the resulting solid polymers were collected and dried in vacuo at 80°C. Polymerization of propene was performed identically at 1 atm of monomer pressure and at 25°C, and the same catalyst and cocatalyst concentration. However, only traces of atactic waxy polymers soluble in toluene were obtained. Polymerization of styrene was carried out similarly, with monomer firstly injected by syringe in the toluene solution, although only traces of atactic solid polymers were obtained.

3.15. X-ray structure determination of 9

Crystallographic and experimental details are given in Table 2. Data collection were performed at 20°C using an Enraf–Nonius CAD4 diffractometer. The structure was solved by Patterson methods and Fourier synthesis, and refined by full-matrix least-squares techniques. Calculations were carried out on a PC486 computer using the SHELXS-86 [53] and SHELX-76 [54] programs. Complex **9** crystallized with a half molecule of benzene. In the Fourier map we found only three atoms of the corresponding molecule, the others being related to them by a symmetrical plane. All the non-hydrogen atoms were refined anisotropically except C3, C4, C26 and the carbon atoms from the solvent. In the later stages of refinement H-atoms were included in calculated positions with fixed thermal parameters using a riding model. A weighting scheme, which gave satisfactory agreement analyses, was introduced in the final cycles of refinement. The final converged agreement factors were $R = 0.087$, $R_w = 0.108$ and $GOF = 1.47$.

Table 2
Crystal, experimental data and structure refinement procedures for compound **9**

Empirical formula	$C_{35}H_{38}SiZr \cdot 1/2 C_6H_6$
Color; habit	Yellow; prismatic
Crystal size(mm)	$0.35 \times 0.25 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 11.268(3) \text{ \AA}$ $b = 10.846(3) \text{ \AA}$ $c = 27.734(6) \text{ \AA}$ $\beta = 100.29(1)^\circ$
Volume	$3334.9(15) \text{ \AA}^3$
Z	4
Formula weight	614.0
Density (calc.)	1.223 g cm^{-3}
Absorption coefficient	0.389 mm^{-1}
$F(000)$	1280
Temperature (K)	292
Index ranges	$-13 < h < 13, -12 < k < 0, 0 < l < 32$
Reflections collected	5992
Observed reflections	2135 ($F > 4.0\sigma(F)$)
Absorption correction	N/A
Solution	Patterson
Refinement method	Full-Matrix Least-Squares
Quantity minimized	$\sum w(F_o - F_c)^2$
Weighting scheme	$W^{-1} = s^2(F) + 0.0020 F^2$
Number of parameters refined	331
Final R indices (obs. data)	$R = 8.66\%$, $R_w = 10.08\%$
R indices (all data)	$R = 23.13\%$, $R_w = 12.80\%$
Goodness-of-fit	1.47
Largest and mean d/s	0.086, 0.004
Largest difference peak	1.27 e \AA^{-3}
Largest difference hole	-102 e \AA^{-3}

4. Synopsis

The synthesis of silyl substituted monocyclopentadienyl zirconium derivatives $[Zr(\eta^5-C_5H_4(SiMe_2X))X_3]$ ($X = NMe_2$, $OSiMe_3$, CH_2CMe_2Ph , C_6H_5 , C_6F_5 , CH_2SiMe_3 and CH_2Ph) by reaction of $[Zr(\eta^5-C_5H_4(SiMe_2Cl))Cl_3]$ with the appropriate alkyl, amido and alkoxo transfer reagent is described. Treatment of $[Zr(\eta^5-C_5H_4(SiMe_2Cl))Cl_3]$ with the salt $Li[C(Ph)\{N(SiMe_3)\}_2]$ leads to the benzamidinate complex $[Zr(\eta^5-C_5H_4(SiMe_2Cl))\{C(Ph)\{N(SiMe_3)\}_2\}Cl_2]$. Reaction of the tetraalkylated compounds with 3 equiv. of HCl gave the corresponding trichloro complexes $[Zr(\eta^5-C_5H_4(SiMe_2R))Cl_3]$ ($R = C_6H_5$, C_6F_5 , CH_2Ph). The monochloro $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))\{CH_2Ph\}_2Cl]$ and the dichloro derivative $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))\{CH_2Ph\}_2Cl_2]$ were identified by NMR spectroscopy. The molecular structure of $[Zr(\eta^5-C_5H_4(SiMe_2CH_2Ph))\{CH_2Ph\}_3]$ has been determined by X-ray diffraction methods.

5. Supplementary material

The supplementary material available includes a complete list of bond distances and angles, anisotropic thermal factors, the calculated fractional coordinates of hydrogen atoms and a list of observed and calculated structure factors.

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